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1,2-Diiodo-, 1,2-dibromo- and 1-bromo-2-iodoperfluoroethanes in 1:1 mixtures with 1,4-dioxane were pressure frozen in a diamond-anvil cell. Structures of cocrystal of 1,2-diiodoperfluoroethane: 1,4-dioxane at 0.30(5) GPa/296(2) K and of 1-bromo-2-iodoperfluoroethane: 1,4-dioxane at 0.62(5) GPa/296 K were determined by single-crystal X-ray diffraction. Also the single-crystal of 1,4-dioxane separated from 1,2-dibromoperfluoroethane, which remained liquid, was investigated at 0.42 GPa/296 K. The cocrystal of $ICF_2CF_2I{:}C_4H_8O_2$ and the 1,4-dioxane crystals are isostructural with their phases frozen by cooling; the $BrCF_2CF_2I{:}C_4H_8O_2$ cocrystal has not been reported earlier. In the structure of $ICF_2CF_2I{:}C_4H_8O_2$ the $–CF_2$-$CF_2$-moiety is disordered about the I···I molecular axis and the $C_4H_8O_2$ molecule rotates about the O···O molecular axis too; and in $BrCF_2CF_2I{:}C_4H_8O_2$ the Br and I atoms are disordered in this way and they possess the same position with half occupancy, but the molecule of $C_4H_8O_2$ is ordered in this complex, and it is also ordered in the structure of the single crystal obtained from the $BrCF_2CF_2Br{:}C_4H_8O_2$ mixture.

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# Halogen···oxygen interactions and disorder modes in pressure frozen complexes of 1,2-dihaloperfluoroethanes with 1,4-dioxane (Preprint)

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**Abstract.** 1,2-Diiodo-, 1,2-dibromo- and 1-bromo-2-iodoperfluoroethanes in 1:1 mixtures with 1,4-dioxane were pressure frozen in a diamond-anvil cell. Structures of cocrystal of 1,2-diiodoperfluoroethane:1,4-dioxane at 0.30(5) GPa/296(2) K and of 1-bromo-2-iodoperfluoroethane:1,4-dioxane at 0.62(5) GPa/296 K were determined by single-crystal X-ray diffraction. Also the single-crystal of 1,4-dioxane separated from 1,2-dibromoperfluoroethane, which remained liquid, was investigated at 0.42 GPa/296 K. The cocrystal of $ICF_2CF_2I$:$C_4H_8O_2$ and the 1,4-dioxane crystals are isostructural with their phases frozen by cooling; the $BrCF_2CF_2I$:$C_4H_8O_2$ cocrystal has not been reported earlier. In the structure of $ICF_2CF_2I$:$C_4H_8O_2$ the -$CF_2$-$CF_2$- moiety is disordered about the I···I molecular

axis and the $C_4H_8O_2$ molecule rotates about the O···O molecular axis too; and in $BrCF_2CF_2I$:$C_4H_8O_2$ the Br and I atoms are disordered in this way and they possess the same position with half occupancy, but the molecule of $C_4H_8O_2$ is ordered in this complex, and it is also ordered in the structure of the single crystal obtained from the $BrCF_2CF_2Br$:$C_4H_8O_2$ mixture.

**Introduction**

Owing to significant differences in physical and chemical properties between fluorine compounds and their hydrogen analogues, haloperfluorocarbons find wide applications in technology, agricultural, and medicine[1]. Recently relatively strong intermolecular interactions of halogen atoms of bromo- or iodoperfluorocarbons with nitrogen, oxygen and sulfur atoms of hydrocarbon Lewis bases were evidenced[2-7]. Complexes of $BrCF_2CF_2Br$, $BrCF_2CF_2I$ or $ICF_2CF_2I$ have been synthesized and their structures determined[2-6]. Also the crystal structures of pure components of these complexes were investigated at low temperature[8-10] and at high pressure[11]. A frequent feature of the dihaloperfluorocarbons and their complexes is the disorder of ethane moieties and Br/I atoms. Owing to the presence of highly electronegative fluorine atoms in haloperfluorocarbons, the halogen atoms acquire a partial positive charge and they form favorably short interactions with electronegative nitrogen or oxygen atoms. Presently we report the results of our investigation on the crystal structures of pressure-frozen mixtures of 1,2-dihaloperfluoroethanes with 1,4-dioxane aimed at revealing their molecular association and origins of disorder in high-pressure condition. The application of pressure was aimed at revealing the compressibility of intermolecular contacts of halogen atoms, identifying the interactions governing the molecular association, eliminating the molecular disorder present in the low-temperature structure of $ICF_2CF_2I$:$C_4H_8O_2$ and determining the thermodynamical conditions favoring the cocrystallizaton of halogen···oxygen complexes.

**Experimental**

**Crystallization of 1,2-diiodoperfluoroethane and 1,4-dioxane:** Liquid $ICF_2CF_2I$ and liquid $C_4H_8O_2$ solidify when mixed at room temperature. The 1:1 cocrystal was melted by heating it to 320 K (its m.p.≈304 K) and in the liquid form loaded to a DAC[12]. After closing the high-pressure chamber the mixture solidified immediately. Then pressure was increased to 0.30 GPa at 296 K, and the DAC was heated to 443 K when the cocrystal melted. By slowly cooling and heating the DAC, a single-crystal was obtained. A strong tendency to kinetic crystallization, resulting in a snowflake-like morphology of crystal, was observed (Figure 1).

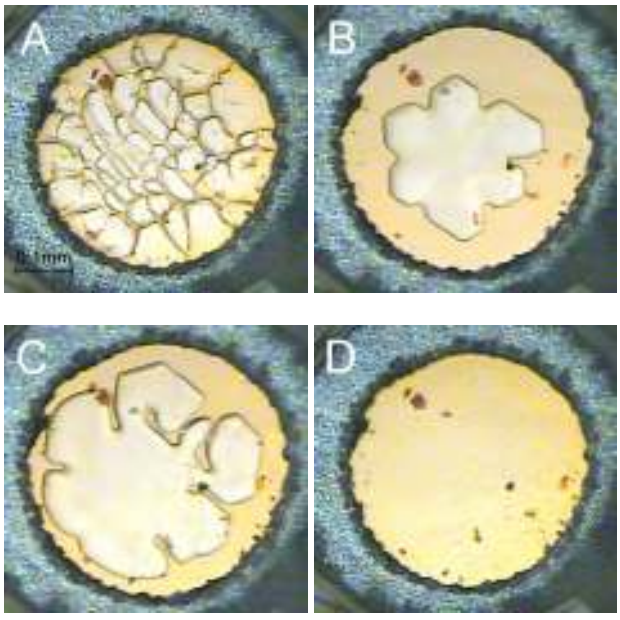


**Figure 1.** Isochoric growth of the 1,2-diiodoperfluoroethane:1,4-dioxane 1:1 cocrystal: (a) the melting process of the polycrystalline sample at 400 K; (b) one single-crystal at 433 K and (c) at 395K; (d) the single-crystal filling the whole volume of the DAC chamber at 296 K. Three small ruby chips for pressure calibration are located at the upper-left corner of the chamber. The yellow stint of the liquid is caused by impurities in the mixture, which condensed at high pressure and grouped between the cocrystal upper face (001) and the upper culet.

**1-Bromo-2-iodoperfluoroethane and 1,4-dioxane co-freezing:** $BrCF_2CF_2I$:$C_4H_8O_2$, 1:1 mol mixture was *in-situ* pressure frozen in a DAC. The freezing pressure of 0.3 GPa has been determined when the polycrystal and liquid were in equilibrium. Then the pressure was increased to 0.6 GPa and the DAC heated till only one grain was left at 390 K. The single-crystal, grown from this seed by slowly cooling the DAC (Figure 2) filled almost the whole chamber volume. The diffraction data were measured for this crystal.

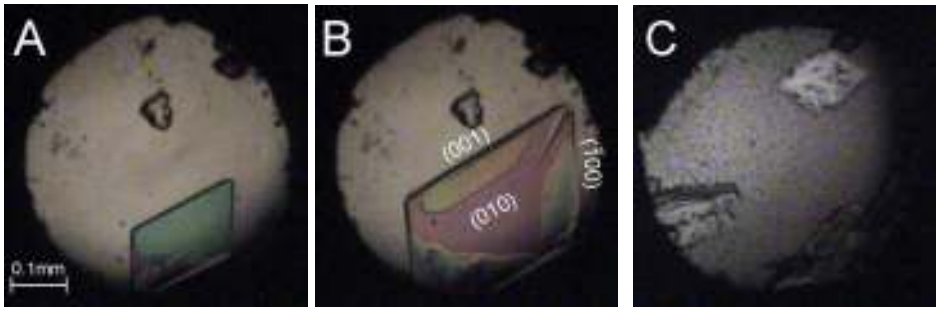


**Figure 2.** Isochoric growth stages of $BrCF_2CF_2I$:$C_4H_8O_2$ cocrystal: (A) a single-crystal seed at 393 K, (B) at 363 K with crystal faces indexed and (C) the cocrystal filling almost the whole volume of the DAC chamber at 296K and 0.62 GPa, except for few small additional crystals–for example the small grain in the upper right edge of the chamber is a twin small of the big crystal according to the mirror plane perpendicular to [100].The ruby chip for pressure calibration, initially above the chamber center (A–B), has been pushed by the cocrystal to the chamber wall (C).

**Crystallization of 1,2-dibromoperfluoroethane and 1,4-dioxane:** The 1:1 mixture of $BrCF_2CF_2Br$ and $C_4H_8O_2$ was loaded in a diamond anvil. Initially these compounds did not completely mix when the liquid was left undisturbed at room temperature: small oil-like drops appeared on the flask walls. Therefore the mixture was shaken till the droplets disappeared before it was loaded in the DAC chamber. After increasing pressure the polycrystalline sample was formed and it was heated till all crystals melted, except one, which was allowed to grow slowly when the DAC chamber was cooled to

296 K. The subsequent X-ray determination confirmed that the single-crystal of 1,4-dioxane was obtained.

Several other attempts to cocrystallize the $BrCF_2CF_2Br$:$C_4H_8O_2$ mixture were undertaken. When pressure was slowly increased isothermally first 1,4-dioxane froze off the solution at about 0.3 GPa and then at about 1.1 GPa 1,2-dibromoperfluoroethane crystallized (Fig. 3). The obtained polycrystalline conglomerate was melted at 513 K. Once one crystal grain appeared, the DAC chamber was slowly cooled to allow it to grow. It was identified by morphology as the 1,4-dioxane crystal. At about 443 K, when the $C_4H_8O_2$ crystal filled half of the DAC chamber, also the crystals of $BrCF_2CF_2Br$ appeared. (Fig. 3 D, E, F). All other attempts to obtain the cocrystal failed, too.

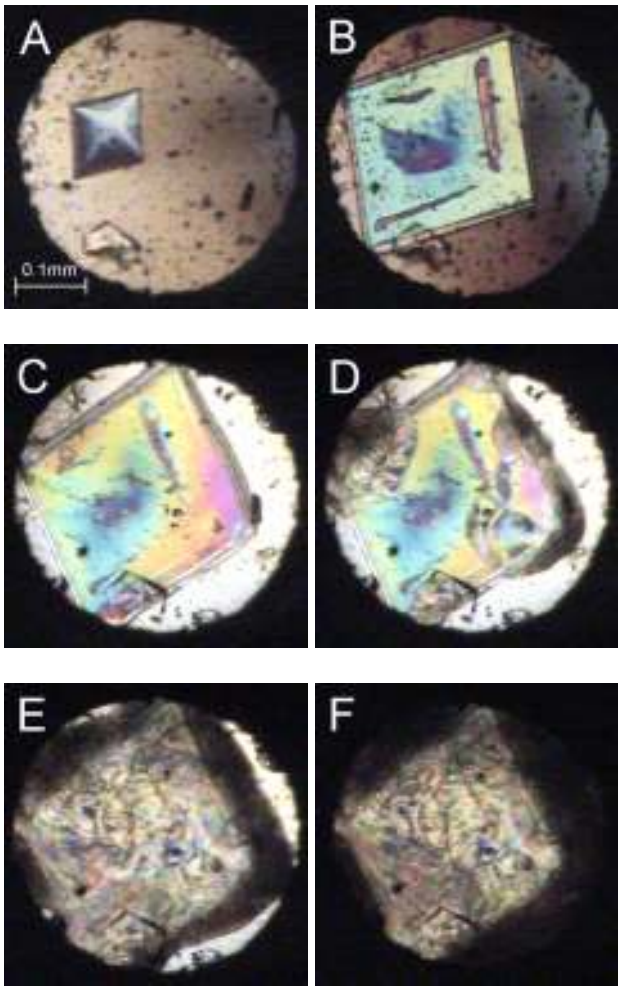

**Figure 3.** Separation of 1,4-dioxane from 1,2-dibromoperfluoroethane:1,4-dioxane mixture by pressure-freezing. (A) One 1,4-dioxane crystal grain left in the DAC chamber at 503 K; (B) this crystal at 483 K with clearly visible faults on its surfaces; (C) the self-repair process of the crystal at 473 K; (D) polycrystalline 1,2-dibromoperfluoroethane appearing at the upper left edge of the chamber at 443 K; and (E, F) the single-crystal of 1,4-dioxane and the polycrystals of 1,2-dibromoperfluoroethane filling the whole volume of the DAC. The ruby chip for pressure calibration is clearly seen above the bottom left edge of the chamber (A).

Pressure in the DAC was calibrated by ruby-fluorescence method,[13,14] using a Betsa PRL spectrometer, with an accuracy of 0.05 GPa. The single-crystal X-ray diffraction studies have been carried out with a KUMA KM4-CCD diffractometer. The CrysAlis version 1.171.24 software[15] was used for the data collections[16] and the preliminary reduction of the data. After the intensities were corrected for the effects of the DAC absorption, sample shadowing by the gasket and the sample absorption[17,18], the diamond reflections have been eliminated. All structures were solved straightforwardly by direct methods[19], and refined by full-matrix least-squares[20]. Anisotropic temperature factors were generally applied, except the structure of $ICF_2CF_2I$:$C_4H_8O_2$, where the isotropic thermal parameters were retained for disordered carbon atoms of $ICF_2CF_2I$ molecule. The crystal data and the structure refinement details are listed in Table 1. Structural drawings were prepared using the X-Seed interface of POV-Ray[21,22]. The GAUSSIAN03 program suite and a PC were used for calculating the electrostatic potential on the molecular surface[23].

**Table 1.** Selected crystal data and details of structure refinement for the $ICF_2CF_2I:C_4H_8O_2$ and $BrCF_2CF_2I:C_4H_8O_2$ cocrystals, and for $C_4H_8O_2$.

| Chemical formula | | $ICF_2CF_2I:C_4H_8O_2$ | $BrCF_2CF_2I:C_4H_8O_2$ | $C_4H_8O_2$ |
|---|---|---|---|---|
| Pressure (GPa) | | 0.30(5) | 0.62(5) | 0.42(5) |
| Temperature (K) | | 296(2) | 296(2) | 296(2) |
| Formula weight | | 441.92 | 394.93 | 88.10 |
| Crystal system | | Trigonal | Monoclinic | Monoclinic |
| Space group | | $R\bar{3}$ | $P2_1/c$ | $P2_1/n$ |
| Unit cell dimensions (Å) | *a* | 8.838(1) | 9.5983(19) | 5.6590(10) |
| | *b* | 8.838(1) | 5.9716(12) | 6.4100(10) |
| | *c* | 13.532(3) | 9.784(2) | 5.8920(10) |
| | *β* | | 107.41(3) | 98.36(3) |
| Volume ($Å^3$) | | 915.4(3) | 535.13(19) | 211.46(6) |
| *Z* | | 3 | 2 | 2 |
| Absorption coefficient ($mm^{-1}$) | | 5.180 | 6.755 | 0.11 |
| *F(000)* | | 606 | 368 | 96 |
| Final $R_1/wR_2$ ($I>2\sigma_1$) | | 0.1335/ 0.3502 | 0.0700/0.1584 | 0.1784 / 0.3250 |
| $R_1/wR_2$ (all data) | | 0.1451 / 0.3668 | 0.0814/0.1651 | 0.2073 / 0.3400 |

**Results and Discussion**

Halogen atoms (Lewis acids, electron acceptor) can interact with atoms containing lone electron pair (Lewis bases)[2-7,24] and this kind of contacts appear in the $ICF_2CF_2I:C_4H_8O_2$ and $BrCF_2CF_2I:C_4H_8O_2$ complexes at high pressure. The electronegative F-atoms considerably change the distribution of electrostatic potential (Figure 4): the positive charge on the I or Br-atoms located axially along their covalent bonds is strongly increased in perfluorated compounds. This explains the linear orientation of

I···O and Br/I···O interactions with respect to their covalent bonds [165.0(3)° and 174(1)° in $ICF_2CF_2I$:$C_4H_8O_2$ and $BrCF_2CF_2I$:$C_4H_8O_2$, respectively].

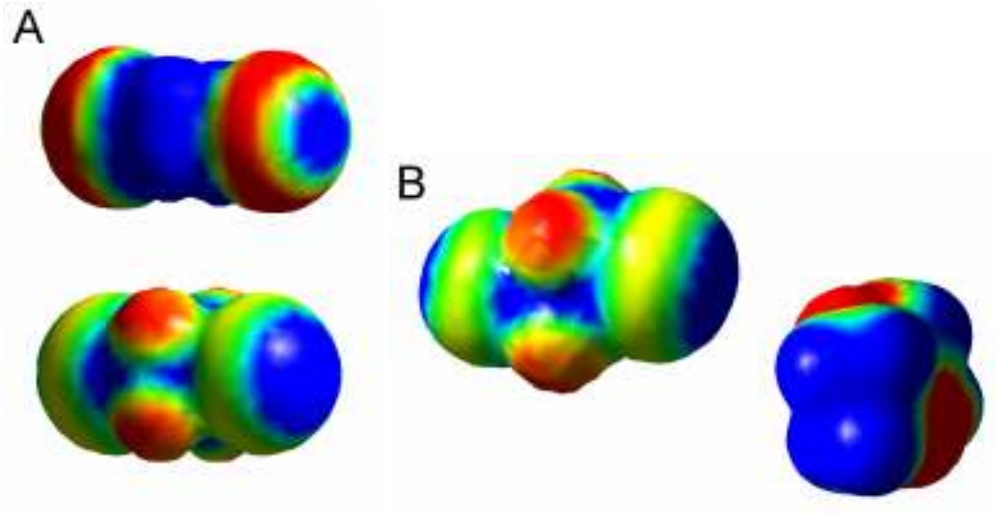


**Figure 4** The molecular surface of $ICH_2CH_2I$ and $ICF_2CF_2I$ (A); $BrCF_2CF_2I$ and $C_4H_8O_2$ (B) with their electrostatic potential indicated in the colour scale, which range from -1 to 1 a.u.

The high-pressure phase of cocrystal $ICF_2CF_2I$:$C_4H_8O_2$ (Table 1) is isostructural with that obtained by cooling[4]. In the low-temperature structure the -$CF_2$-$CF_2$- group in 1,2-diiodoperfluoroethane rotates about I···I molecular axis and -$CH_2$-$CH_2$- ethylene unit in 1,4-dioxane are disordered around the O···O axis. At high-pressure the $ICF_2CF_2I$ and $C_4H_8O_2$ molecules are disordered in the same manner. Also in the structure of pure $ICF_2CF_2I$ the molecules rotate below 0.86 GPa[11]. In $ICF_2CF_2I$:$C_4H_8O_2$ the shortest intermolecular interactions I···O dominate the molecular association in crystal. At 0.3 GPa the I···O distance is of 3.136(54) Å, and at 0.1MPa/200 K this distance is shorter by 0.322 Å. The I···O interactions link the molecules into chains along the [001] direction, as shown in Fig. 5. The C–I···O angles are 163.3° and 165.0(3)º at low temperature and high pressure, respectively. The shortest I···I distance of 5.138(2) Å is much longer than the I···O contacts. Ordered I- and O-atoms testify that the I···O interactions are the strongest in this structure. The distances of I atoms to the sites of disordered F atoms are of 3.933 Å at low temperature and they are squeezed by 0.76 Å at high pressure. The shortest

intermolecular distance of two F atoms are significantly longer than the sum of Van der Waals radii[25] of these atoms in both phases, and it is 4.63(8) Å and 4.725 Å. The molecular packing of $ICF_2CF_2I:C_4H_8O_2$ at 0.3 GPa is presented in Figure 5, and the intermolecular distances in Table 2.

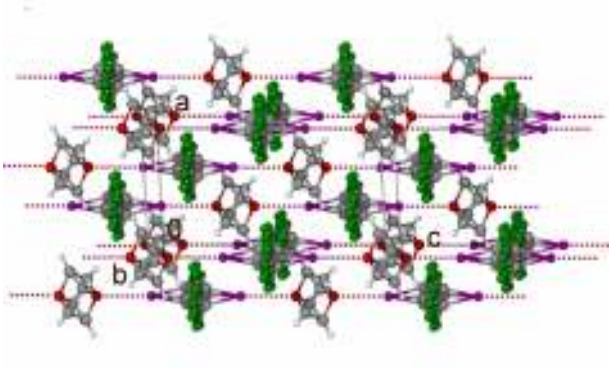


**Figure 5.** The molecular packing of 1,2-diiodoperfluoroethane:1,4-dioxane cocrystal at 0.30GPa/296K. The shortest I···O contacts have been indicated as dashed lines, and the disordered sites of the $-CF_2-CF_2-$ and $-CH_2-CH_2-$ moieties have been shown.

In the structure of 1-bromo-2-iodoperfluoroethane:1,4-dioxane cocrystal the $-CF_2-CF_2-$ and $-CH_2-CH_2-$ moieties are ordered. However, another type of disorder appears: the $BrCF_2CF_2I$ and $C_4H_8O_2$ molecules are each located at the center of inversion, hence the Br and I atoms are disordered and located at the same or very close site with a half occupancy. The different types of disorder in $BrCF_2CF_2I:C_4H_8O_2$ and $ICF_2CF_2I:C_4H_8O_2$ cocrystals can be explained by the molecular interactions. In both complexes short X···O (X=Br or Br/I) contacts are present and they dominate these structures. However, in $BrCF_2CF_2I:C_4H_8O_2$ the X···O contact is about 0.2 Å shorter than in $ICF_2CF_2I:C_4H_8O_2$. Each molecule of the $BrCF_2CF_2I:C_4H_8O_2$ forms two Br/I···O contacts of 2.93(2) Å, which arrange molecules into chains along the [110] direction. The next shortest Br/I···O distance is about 0.9 Å longer. The Br/I···F interactions are very weak, and the closest contact is of 3.73(2) Å, while in $ICF_2CF_2I:C_4H_8O_2$ the I···F contacts are 0.56 Å shorter. However, the F···F contacts are significantly shorter in $BrCF_2CF_2I:C_4H_8O_2$ [2.74(2) Å and 4.63(8) Å for $BrCF_2CF_2I:C_4H_8O_2$ and $ICF_2CF_2I:C_4H_8O_2$,

respectively]. These F···F interactions can hinder the $–CF_2–CF_2–$ group rotations in the $BrCF_2CF_2Br$ molecule. Moreover, in $BrCF_2CF_2I{:}C_4H_8O_2$ relatively short O···H intermolecular contacts are present, which can be responsible for ordering the $C_4H_8O_2$ molecules. These O···H contacts are by over 1 Å shorter in this complex than in $ICF_2CF_2I{:}C_4H_8O_2$. Each 1,4-dioxane molecule in $BrCF_2CF_2I{:}C_4H_8O_2$ interacts forming O···H hydrogen bonds, analogous to those observed in the 1,4-dioxane phase II (see below). The shortest O···H contacts of 2.592 Å and 2.943 Å link the 1,4-dioxane molecules along to the (100) planes (Table 2, Figure 6).

It can be concluded, that the I···O and Br/I···O interactions govern the molecular arrangement in the complexes with 1,4-dioxane, and that these interactions replace the I···I and Br/I···Br/I contacts in $ICF_2CF_2I{:}C_4H_8O_2$ and $BrCF_2CF_2I{:}C_4H_8O_2$ (Table 2). The substitutional Br/I disorder in $BrCF_2CF_2I{:}C_4H_8O_2$ is analogical to that observed in pure $BrCF_2CF_2I$ crystals. Thus the Br/I disorder is a characteristic feature of many symmetrical compounds, resulting from the small difference of about 0.2 Å between van der Waals radii of Br and I atoms (1.95 Å for Br *vs.* 2.15 Å for I).[25]

The 1,4-dioxane molecules in $BrCF_2CF_2I{:}C_4H_8O_2$ form sheets very similar to those observed in low-temperature phase II of pure 1,4-dioxane. We found, that pressure-frozen 1,4-dioxane crystallizes in phase II, too. For comparing the 1,4-dioxane sheets in $BrCF_2CF_2I{:}C_4H_8O_2$ with those in 1,4-dioxane phase II, we determined the crystal structure of 1,4-dioxane at 0.42 GPa (Figure 6).

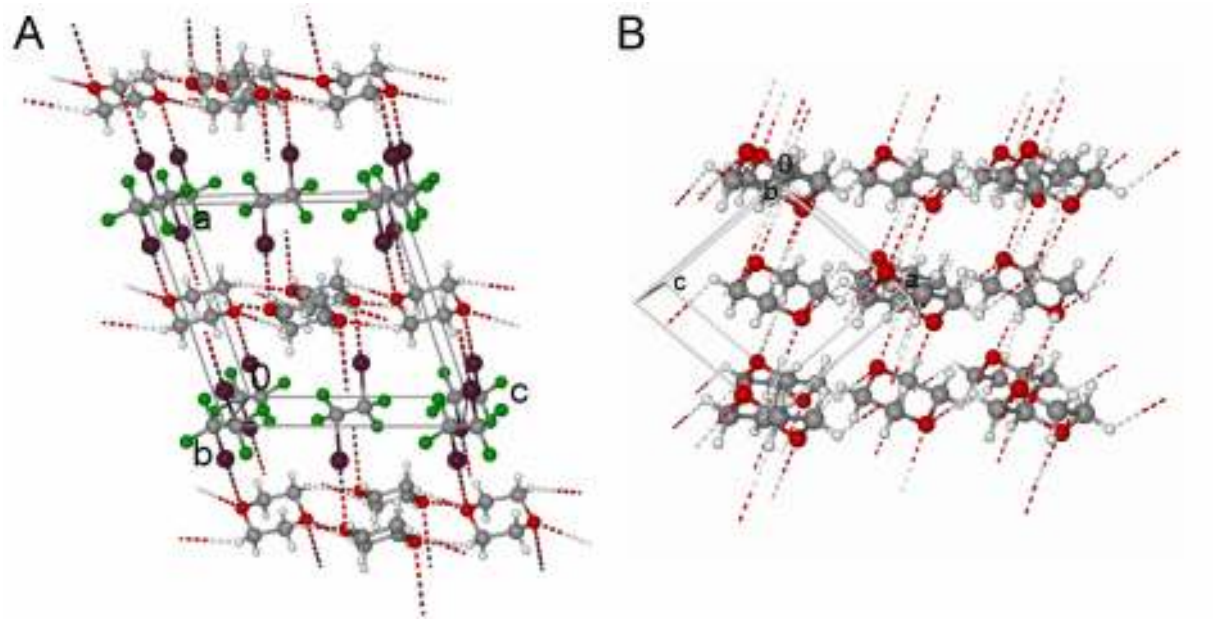


**Figure 6.** The molecular packing of (A) 1,2-dibromoperfluoro:1,4-dioxane cocrystal with the shortest Br/I···O interactions of 2.93(2) Å and O···H of 2.592 Å at 0.62 GPa/296 K; and (B) 1,4-dioxane with two shortest O···H contacts of 2.655 Å and 2.672 Å at 0.42 GPa/296 K.

There are no intermolecular interactions shorter than the sums of van der Waals radii in all 1,4-dioxane phases: the shortest contact can be observed in the structure of phase II at 0.42 GPa: O···O of 3.59 Å and two shortest O···H contacts about 2.7 Å (Table 3). The O and H atoms interact forming sheets along the crystal $(0\bar{1}1)$ and $(01\bar{1})$ plane as can be seen in Figure 6 and the intermolecular interactions.

When assuming strong I···O and weak Br···O interactions, the $BrCF_2CF_2I$:$C_4H_8O_2$ cocrystal can be considered as a disordered mixed cocrystal built of:

- 1:1 aggregates $BrCF_2CF_2I$···$C_4H_8O_2$ in two orientations inconsistent with the crystal symmetry; and
- 2:1 aggregates $BrCF_2CF_2I$···$C_4H_8O_2$···$ICF_2CF_2Br$ and of $C_4H_8O_2$ having short contacts with Br atoms only.

Nonetheless, these I···O interactions are strong enough to secure cohesion of the $BrCF_2CF_2I$:$C_4H_8O_2$ cocrystal.

**Table 2.** The shortest contacts in high-pressure structure of 1,2-diiodoperfluorethane:1,4-dioxane and 1-bromo-2-iodoperfluoroethane:1,4-dioxane.

| $ICF_2CF_2I$:$C_4H_8O_2$ | | $BrCF_2CF_2I$:$C_4H_8O_2$ | |
|---|---|---|---|
| p (GPa)/T (K) | 0.30/296 | | 0.62/296 |
| I···$I^{i,ii,iii}$(Å) | 5.138(2) | Br/I···Br/$I^{i}$(Å) | 4.612(7) |
| I···$O^{iv}$ | 3.14(5) | Br/I···$O^{ii}$ | 2.93(2) |
| I···$O^{v,vi,vii}$ | 5.16(7) | | |
| I···$F^{viii,ix,x}$ | 3.17(4) | Br/I···$F^{iii}$ | 3.73(2) |
| I···$F^{viii,ix,x}$ | 3.18(2) | Br/I···$F^{iv}$ | 3.92(3) |
| F···$F^{xi}$ | 4.63(8) | F···$F^{v}$ | 2.74(2) |
| | | F···$F^{vi}$ | 2.74(2) |
| O···$H^{xii,xii,xiv}$ | 3.862 | O···$H^{vii}$ | 2.592 |
| C-I···$I^{i}$ (°) | 70.1(3) | C-Br/I···Br/$I^{i}$ (°) | 74(1) |
| C-I···$I^{ii}$ | 84.1(2) | C-Br/I···$O^{ii}$ | 174(1) |
| C-I···$I^{iii}$ | 96.0(4) | C-Br/I···$F^{iv}$ | 110(1) |
| C-I···$O^{iv}$ | 165.0(3) | C-Br/I···$F^{v}$ | 63.4(8) |
| C-I···$O^{v}$ | 85.9(6) | C-F···$F^{v}$ (°) | 161(3) |
| C-I···$O^{vi}$ | 97.8(5) | C-F···$F^{vi}$ | 118(3) |
| C-I···$O^{vii}$ | 111.8(5) | C-O···$H^{vii}$ | 92.42 |
| C-I···$F^{viii}$ | 44.4(7) | | |
| C-I···$F^{ix}$ | 18.6(7) | | |
| C-I···$F^{x}$ | 36.5(8) | | |
| C-I···$F^{viii}$ | 49.5(4) | | |
| C-I···$F^{ix}$ | 28.1(5) | | |

| | |
|---|---|
| C-I···F$^{x}$ | 31.3(5) |
| C-F···F$^{xi}$ | 103.6(6) |
| C-O···H$^{xii}$ | 68.28 |
| C-O···H$^{xiii}$ | 118.22 |
| C-O···H$^{xiv}$ | 138.66 |

Symmetry codes: i: 5/3-x, 4/3-y, 4/3-z; ii: 5/3-x, 7/3-y, 4/3-z; iii: 8/3-x, 7/3-y, 4/3-z; iv: -x+2, -y+2, -z+1; v: -2/3+x, -1/3+y, 2/3+z; vi: 1/3+x, -1/3+y, 2/3+z; vii: 1/3+x, 2/3+y, 2/3+z; viii: -x+2, -y+2, -z+1; ix: y, -x+y+1, -z+1; x: x-y+1, x, -z+1; xi: 5/3-x, 4/3-y, 4/3-z; xii: 5/3-x, 7/3-y, 1/3-z; xiii: -1/3+y, 1/3-x+y, 1/3-z; xiv: 5/3+x-y, 1/3+x, 1/3-z

Symmetry codes: i: -x,-y,-z+1; ii: -x+1,-0.5+y,-z+1.5; iii: -x,-y,-z+1; iv: -x,-0.5+y,-z+1.5; v: -x, 0.5+y, 1.5-z; vi: -x, -0.5+y, 1.5-z; vii: x, 0.5-y, -0.5+z

**Table 3.** The shortest contacts in the structure of phase II of 1,4-dioxane at 0.42 GPa.

| | $C_4H_8O_2$ |
|---|---|
| p (GPa)/T (K) | 0.42/296 |
| O···H$^{i}$ (Å) | 2.655 |
| O···H$^{ii}$ | 2.672 |
| C-O···H$^{i}$ (°) | 88.35 |
| C-O···H$^{ii}$ | 86.06 |

Symmetry codes: i: 0.5+x, 1.5-y, 0.5+z; ii: 1.5-x, 0.5+y, 0.5-z

**Conclusions.** The high-pressure studies on 1,2-dihaloperfluoroethanes:1,4-dioxane, 1:1 mol, complexes revealed the molecular disorder, the patterns of intermolecular interactions and the ability of

I and Br/I atoms to form short contacts with oxygen. However, the Br···O contacts have not been observed as pure $BrCF_2CF_2Br$ does not cocrystallize with $C_4H_8O_2$. The pressure freezing of $BrCF_2CF_2Br$:$C_4H_8O_2$, 1:1 mixture, resulted in a single crystal of $C_4H_8O_2$ at 0.42 GPa and 296K (see Experimental). At these conditions $CF_2BrCF_2Br$ remains liquid. The formation of the $BrCF_2CF_2Br$:$C_4H_8O_2$ cocrystal could be additionally hampered by the big difference in melting points of 161.65 K for $BrCF_2CF_2Br$[26] and 285 K for $C_4H_8O_2$.

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**Supporting Information Available**. Crystallographic information files (CIF) and the tables of crystal data and refinement details for inclusion compounds are available at http://pubs.acs.org.

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